

Supporting Information for

Cooperative Electronic- and Structural-Regulation in a Bioinspired Allosteric Photoredox Catalyst

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TITRATIONS

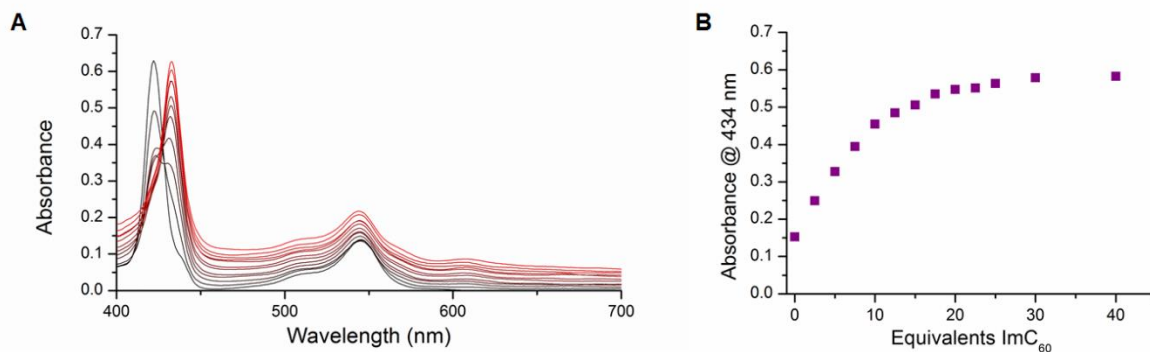


Figure S1. UV-vis titration of **ImC₆₀** from a concentrated 1,2-dichlorobenzene solution into a 1 μ M solution of **1** in CH₂Cl₂: absorption spectral changes (A) and absorbance changes at 434 nm following titration (B).

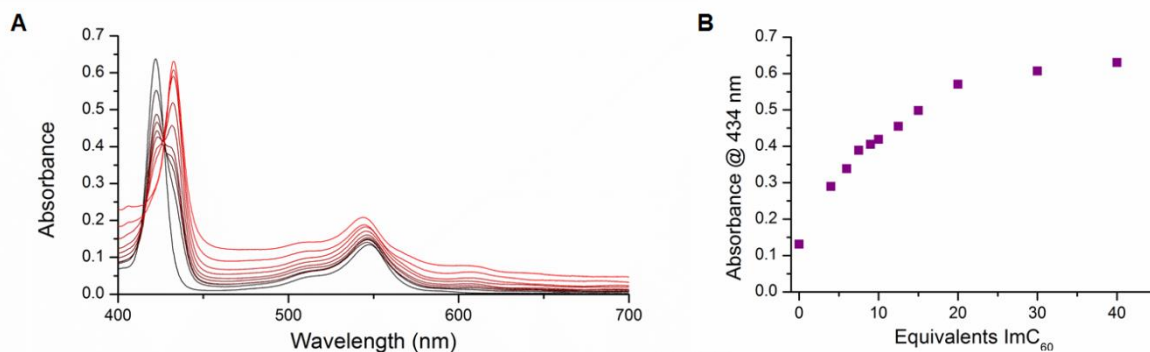


Figure S2. UV-vis titration of **ImC₆₀** from a concentrated 1,2-dichlorobenzene solution into a 1 μ M solution of **2** in CH₂Cl₂: absorption spectral changes (A) and absorbance changes at 434 nm following titration (B).

REVERSIBILITY OF ALLOSTERICALLY-INDUCED STRUCTURAL CHANGES

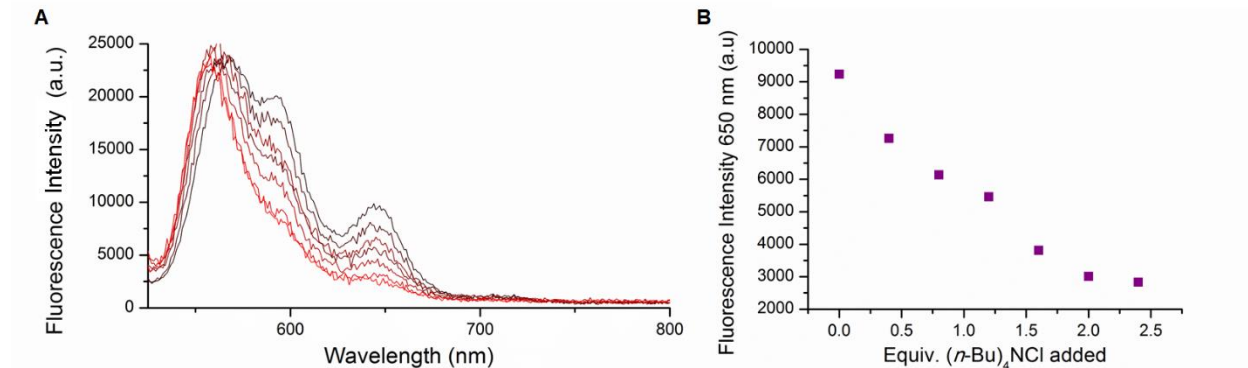


Figure S3. Fluorescence spectral changes following titration of N(n-Bu)₄Cl into a 1 μ M solution of **1** in CH₂Cl₂ (A) and associated changes in fluorescence intensity at 650 nm.

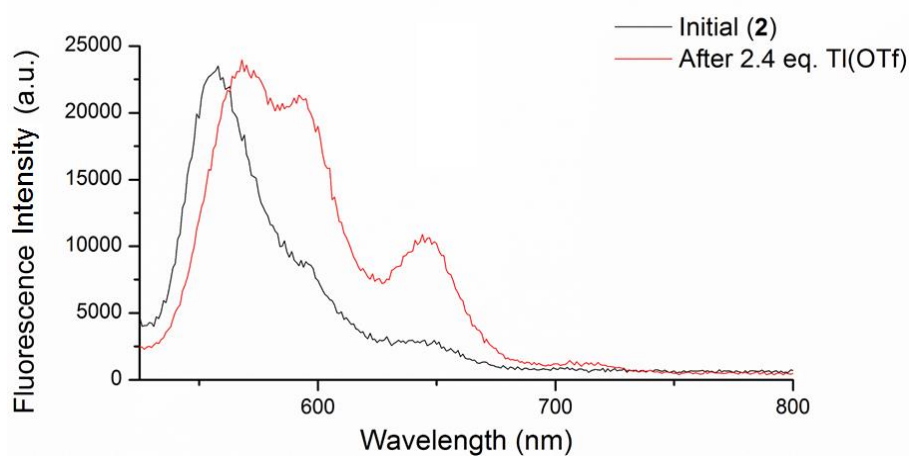


Figure S4. Fluorescence spectral changes following addition of 2.4 eq. of Tl(OTf) into a 1 μ M solution of **2** in CH₂Cl₂.

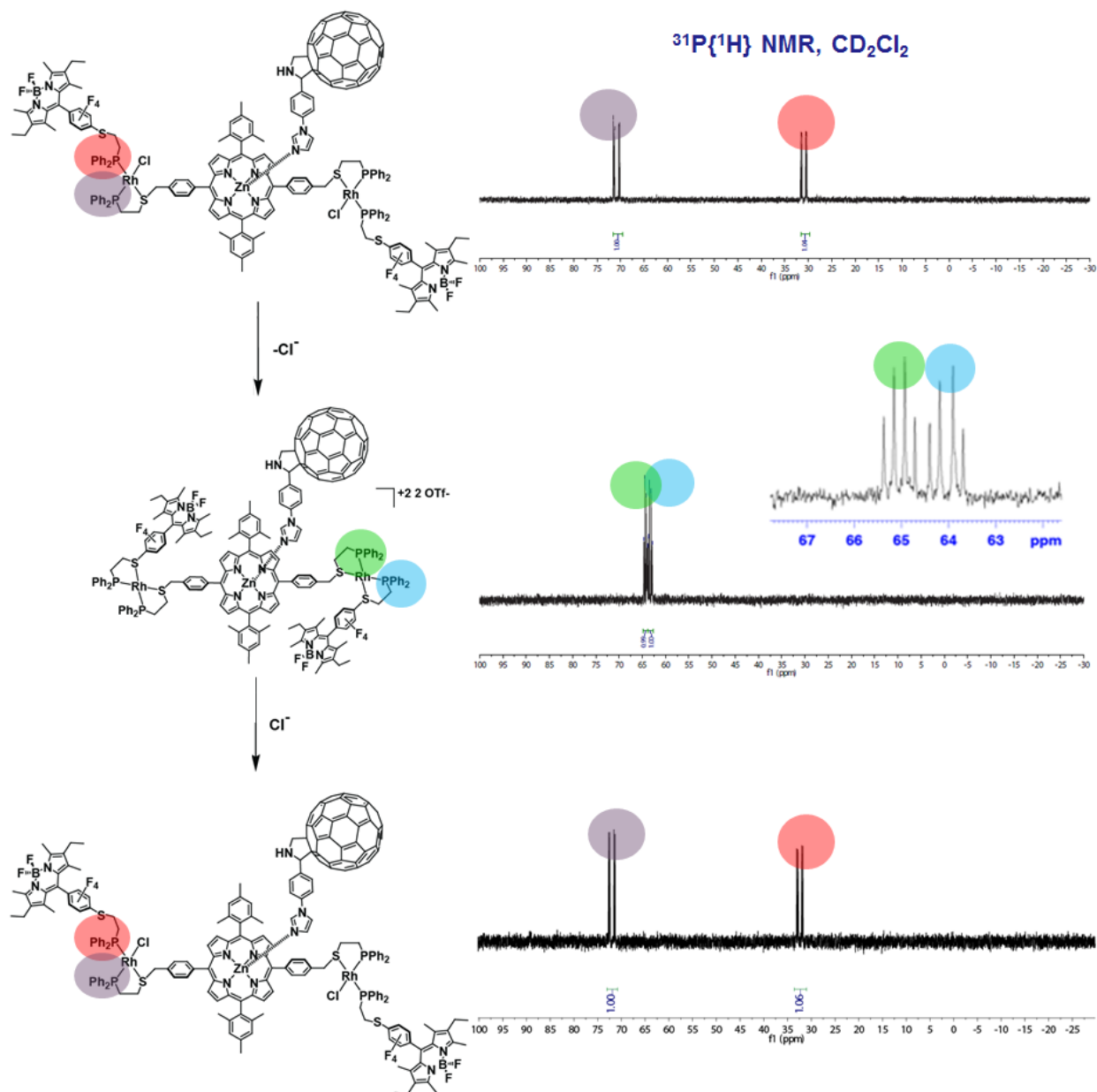


Figure S5. *In situ* toggling between coordination states tracked by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

The spectra represent 1 mM solutions of complexes **1-2** in the presence of 10 equiv. of **ImC₆₀**.

COMPUTATIONAL

DFT calculations were performed using the Amsterdam Density Functional (ADF2013.01) suite on a 16-core Parallel Quantum Solutions (PQS) computational cluster. The model for complex **1** was initially based on the crystallographic coordinates of its solid-state structure. Geometry optimizations were made without restraint in the ADF GUI using basis sets containing triple- ζ functions with two polarization function (TZ2P), and the local density approximations of Becke¹ and Perdew.² This was followed by single point calculations using triple- ζ functions with two polarization functions (TZ2P) and the PBE-hybrid (PBE0) functional by Ernzerhof-Scuseria¹ and by Adamo-Barone.² Kohn-Sham representations of frontier orbitals were generated by the ADF 2013.01 GUI. Electron density plots with electron density potential mapped onto them for complexes **1** and **2** were calculated at the PBE-hybrid (PBE0) level of theory and mapped with the 0.03 e⁻/Å³ isodensity value.

Single point calculations of the orbital energy levels of complexes **1** and **2** show that coordination of chloride to Rh^I raises the metal's d_{z^2} orbital energy and places it between the antenna frontier orbitals, thus giving rise to quenching via PeT in the excited state. The relative energy levels follow the same order established via electrochemical characterization.

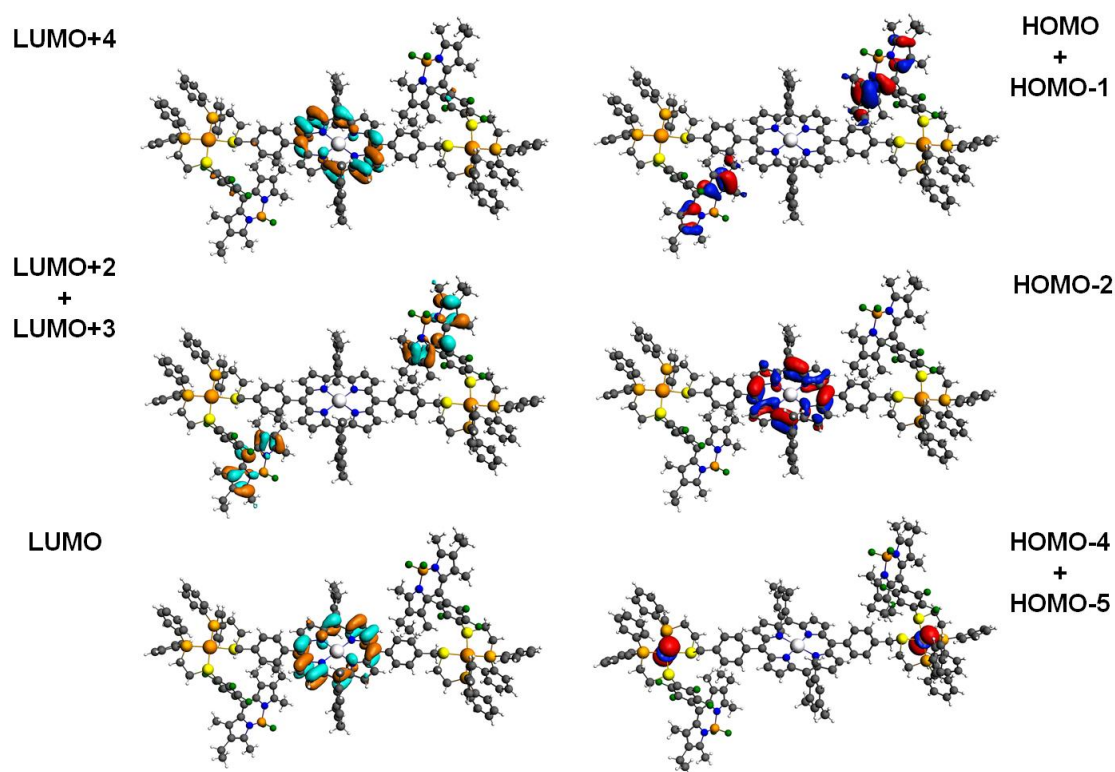


Figure S6. Theoretical modeling of frontier orbitals in complex **1** determined via single point DFT calculations.

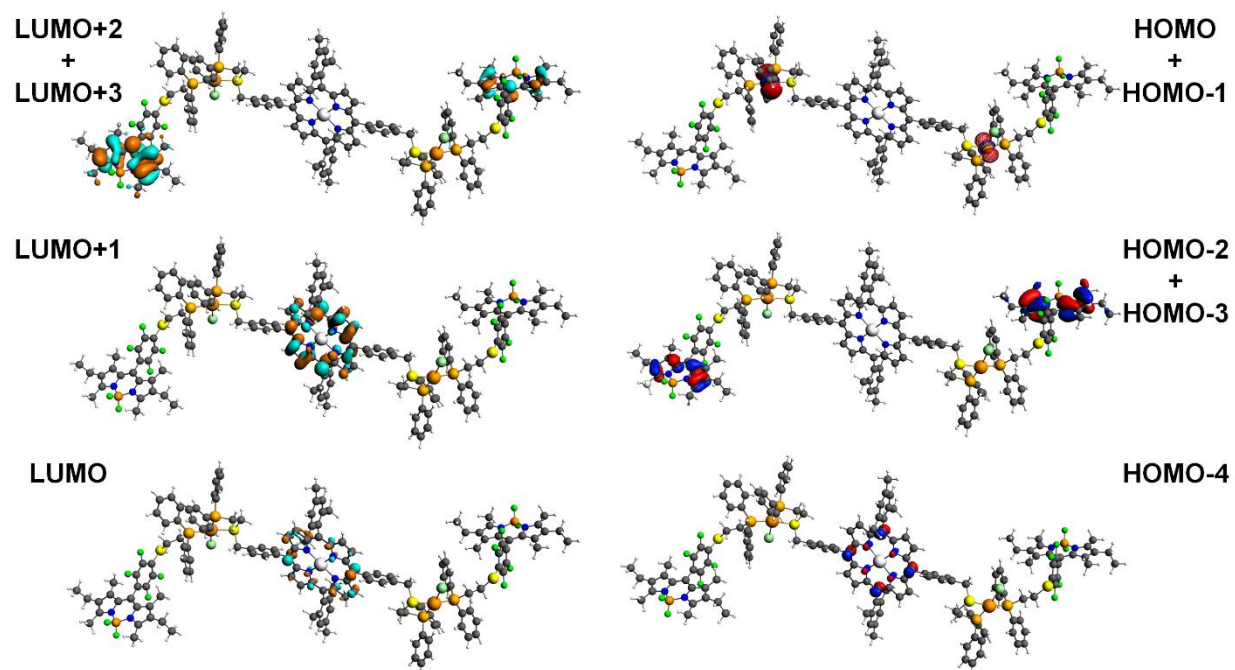


Figure S7. Theoretical modeling of frontier orbitals in complex **2** determined via single point DFT calculations.

TRANSIENT ABSORPTION SPECTRA

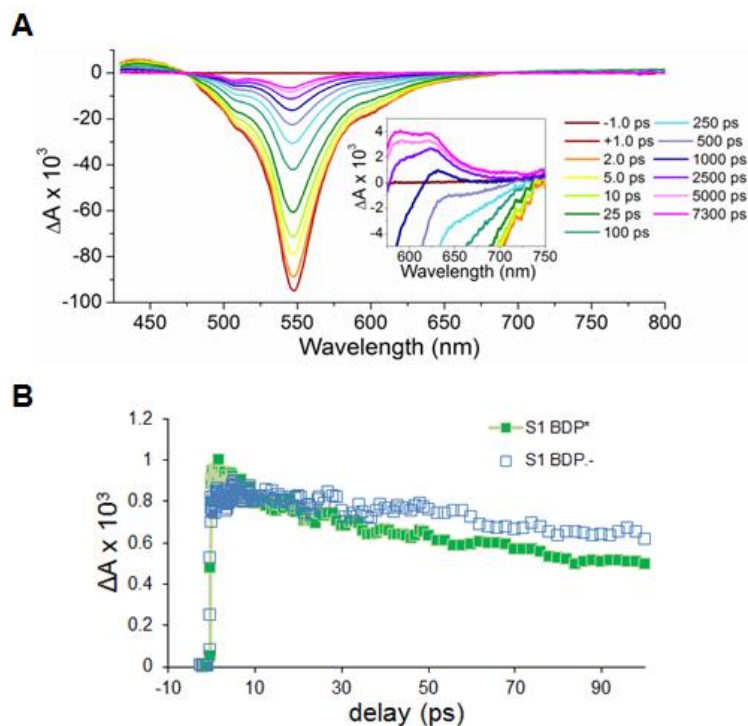


Figure S8. Kinetics of PET from Rh^{I} to Bodipy: (A) Previously reported transient absorption spectra of complex **M2** in CH_2Cl_2 ($\lambda_{\text{ex}} = 505 \text{ nm}$) with inset highlighting formation of the Bodipy radical anion.³ (B) Deconvoluted kinetic profiles corresponding to decays of singlet excited Bodipy ($\lambda_{\text{abs}} = 445 \text{ nm}$) and the Bodipy radical anion ($\lambda_{\text{abs}} = 600 \text{ nm}$) following excitation.

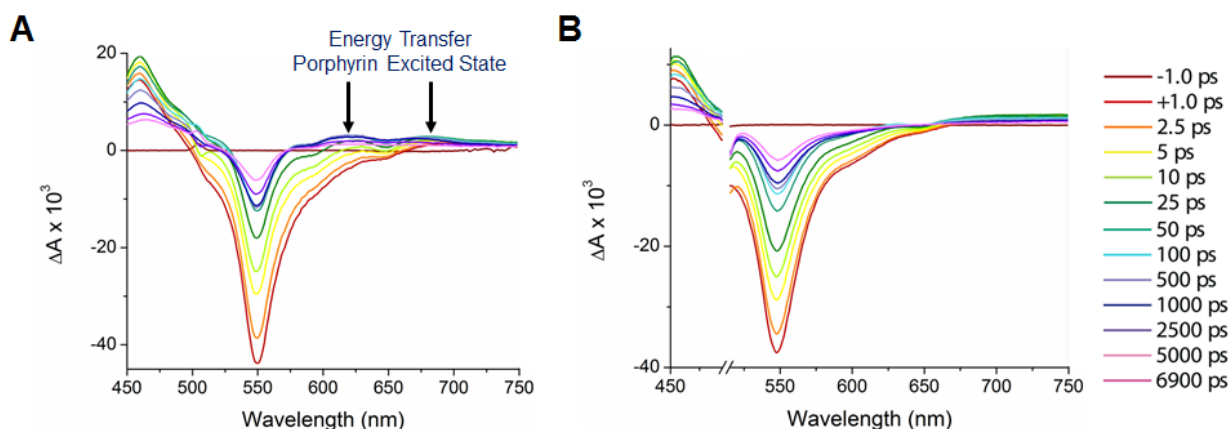


Figure S9. Transient absorption spectra of 3 μM solutions of **1** (A) and **2** (B) with 1.1 μJ laser pulses in CH_2Cl_2 ($\lambda_{\text{ex}} = 505 \text{ nm}$).

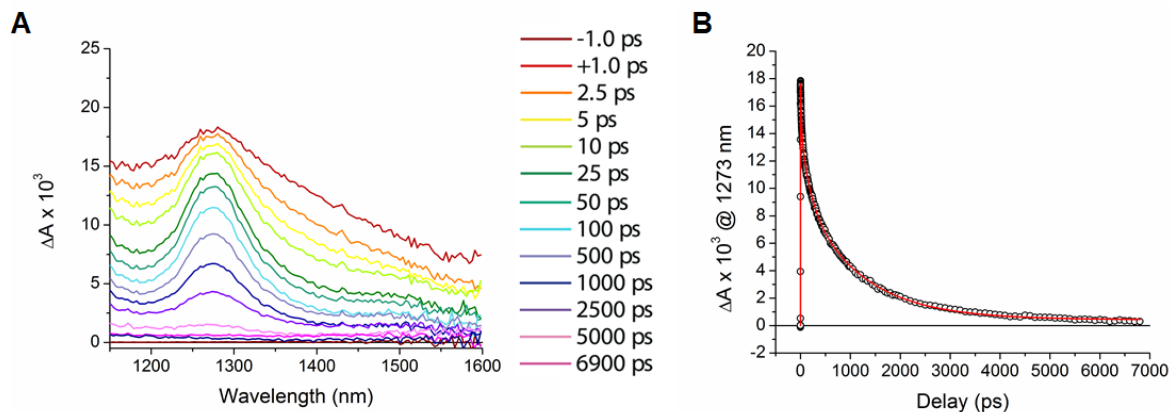


Figure S10. NIR transient absorption spectra of 3 μM solutions of **1** in CH_2Cl_2 resulting from direct excitation of the porphyrin (A, $\lambda_{\text{ex}} = 550 \text{ nm}$) and kinetic fit of changes in transient absorption at 1283 nm characteristic of the porphyrin excited state (B).

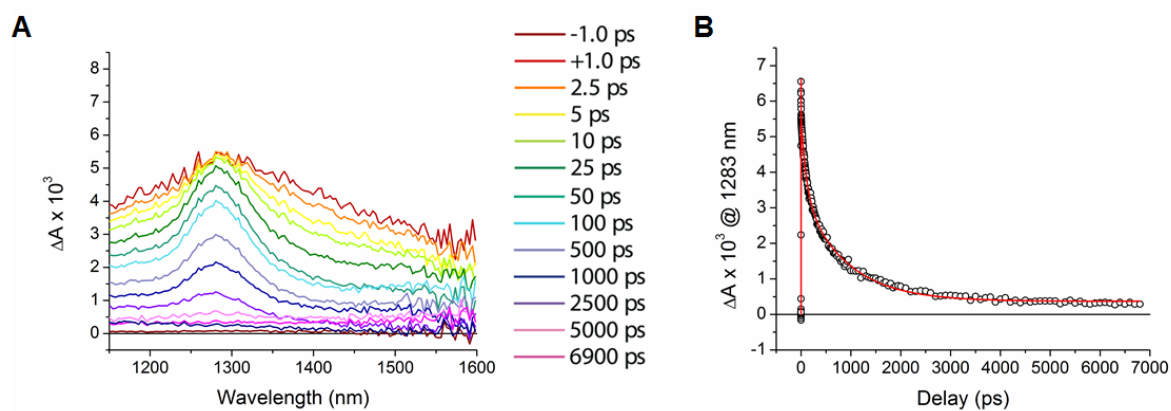


Figure S11. NIR transient absorption spectra of 3 μM solutions of **2** in CH_2Cl_2 resulting from direct excitation of the porphyrin (A, $\lambda_{\text{ex}} = 550 \text{ nm}$) and kinetic fit of changes in transient absorption at 1273 nm characteristic of the porphyrin excited state (B).

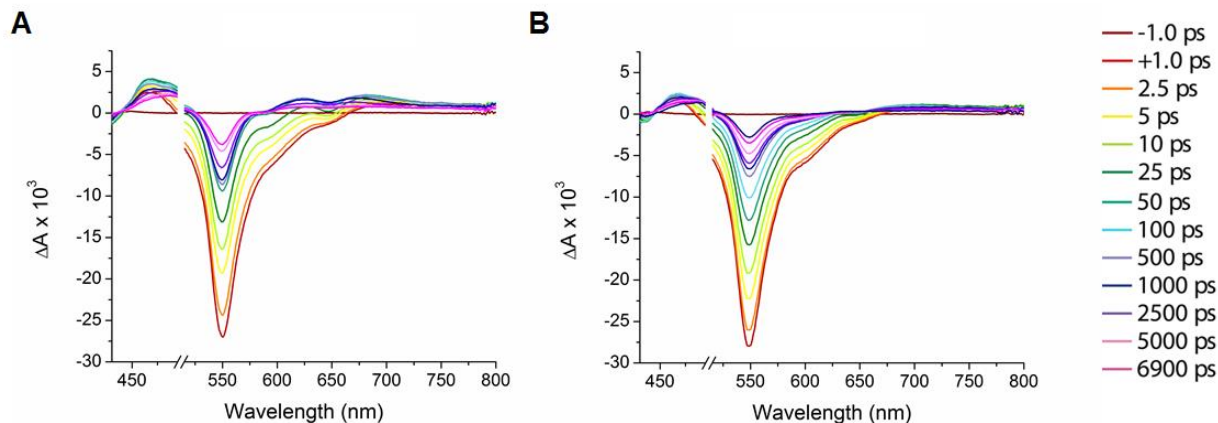


Figure S12. Transient absorption spectra of **(1-2)-ImC₆₀**. Excitation of 3 μM solutions of **1** (A), **2** (B) with 1.1 μJ laser pulses in the presence of 10 eq. of ImC₆₀ in CH₂Cl₂ (λ_{ex} = 505 nm).

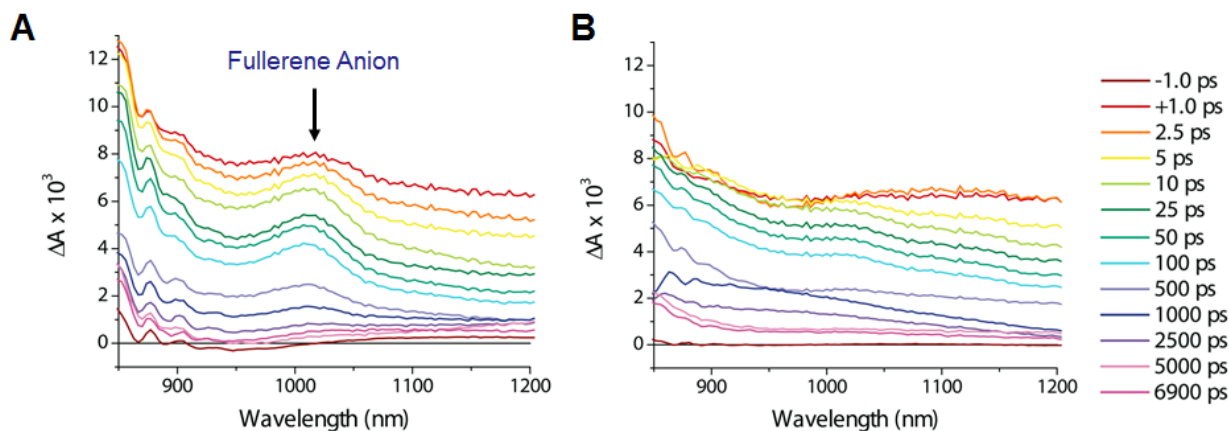


Figure S13. NIR-transient absorption spectra of **(1-2)-ImC₆₀**. Excitation of 3 μM solutions of **1** (A), **2** (B) with 1.1 μJ laser pulses in the presence of 10 eq. of ImC₆₀ in CH₂Cl₂ (λ_{ex} = 505 nm).

Table S1. Optical and Kinetic Data.^a

| Complex | λ_{max} Bodipy (nm) | $\lambda_{\text{fluor. em.}}$ Bodipy (nm) | $\tau_{\text{Bodipy}}^* \text{ (s)}$ (Amplitude %) | $\tau_{\text{ZnPorphyrin}}^* \text{ (s)}$ (Amplitude %) | Q.Y. |
|-----------|------------------------------------|---|---|--|-------|
| 1 | 545 | 565 | $(9.60 \pm 0.54) \times 10^{-11}$ (96%) | $(1.15 \pm 0.08) \times 10^{-9}$ (76%) | 0.026 |
| 2 | 548 | 557 | $(6.46 \pm 0.37) \times 10^{-11}$ (77%) | $(9.85 \pm 1.38) \times 10^{-10}$ (69%) | 0.017 |
| S1 | 547 | 569 | $(3.56 \pm 0.17) \times 10^{-10}$ (99%) | - | 0.48 |
| S2 | 544 | 571 | $(6.92 \pm 0.46) \times 10^{-11}$ (92%) | - | 0.089 |

^a Excited State half-life values were calculated from kinetic fits of the TA data.

PHOTOREDOX CATALYSIS

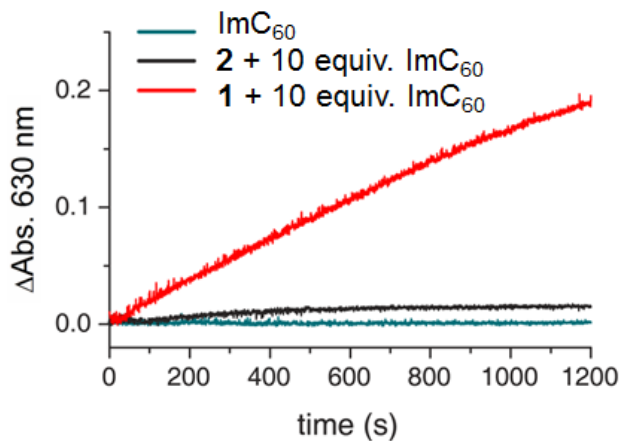


Figure S14. Catalytic reduction of methyl viologen in the presence of 1 μM **1** or **2** and 10 eq. of **ImC₆₀** and control experiment in the absence of Rh^{I} complex: changes in absorbance at 630 nm ($\lambda_{\text{ex}} = 505 \text{ nm}$, 0.8 mW) in CH_2Cl_2 .

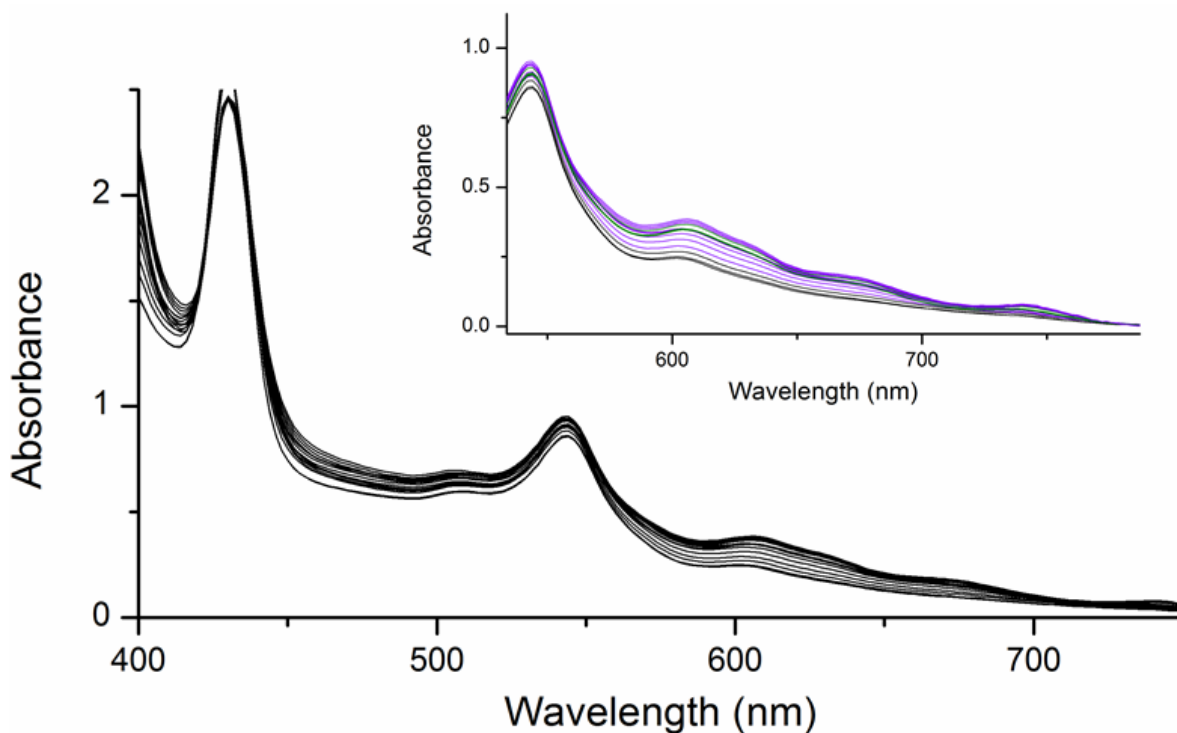


Figure S15. Absorption spectral changes following allosteric regulation of the reduction of methyl viologen in the presence of 5 μM **1** and 10 eq. of **ImC₆₀** ($\lambda_{\text{ex}} = 505 \text{ nm}$, 0.2 mW, CH_2Cl_2). Inset: before excitation (black), excitation (purple), addition of 2 equiv. of $(n\text{-Bu})_4\text{NCl}$ (green), and addition of 6 eq. of TlOTf (purple).

OPTICAL SPECTRA

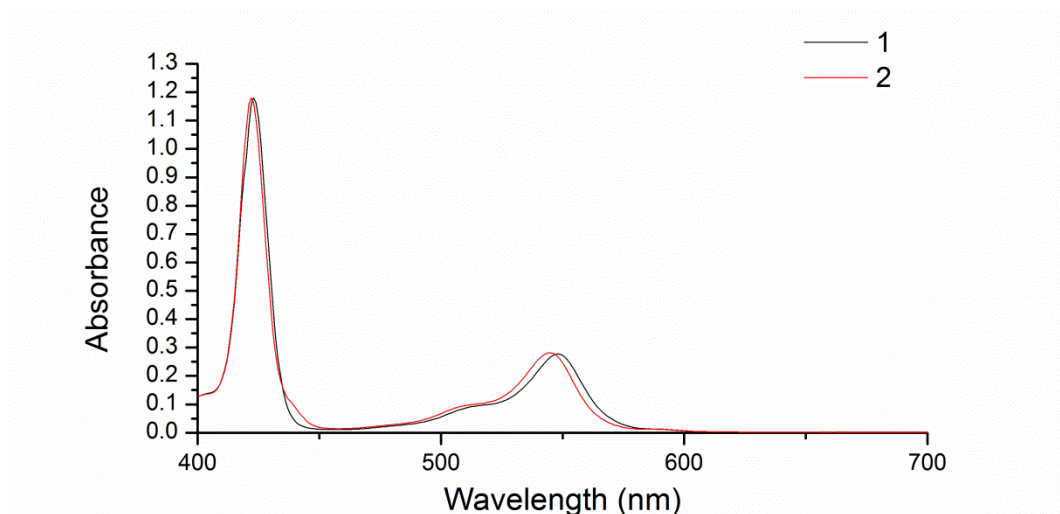


Figure S16. UV-vis spectra of 2 μM solution of **1** and **2** in CH_2Cl_2 .

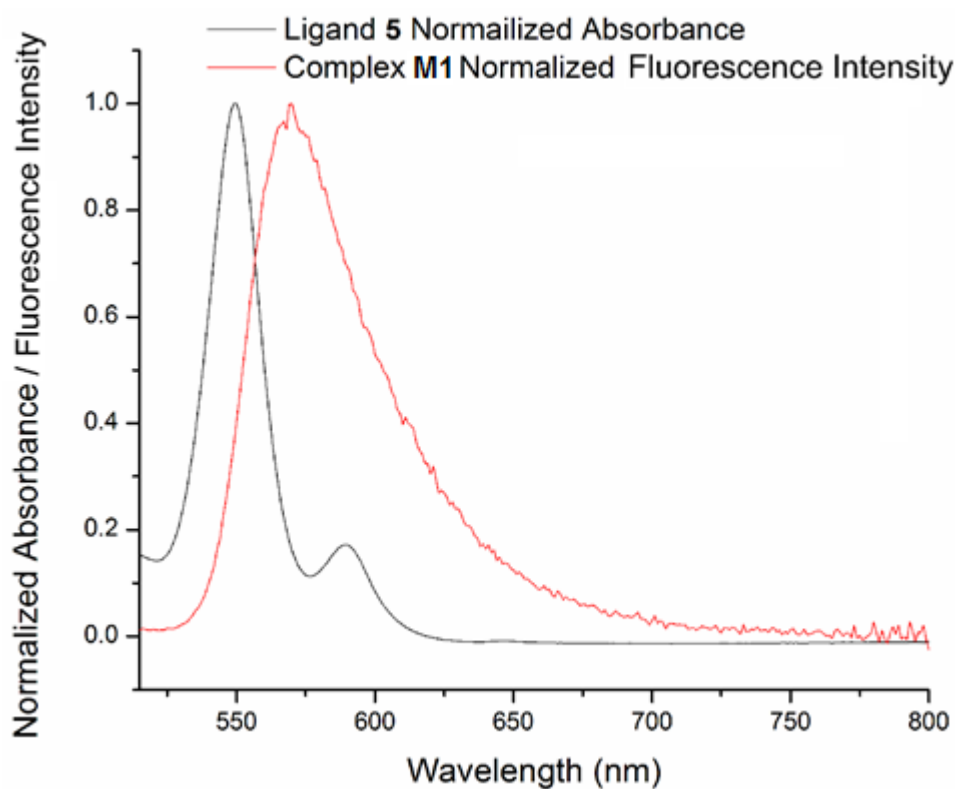


Figure S17. Normalized UV-vis spectrum of **5** and normalized fluorescence spectrum of **M1** in CH_2Cl_2 .

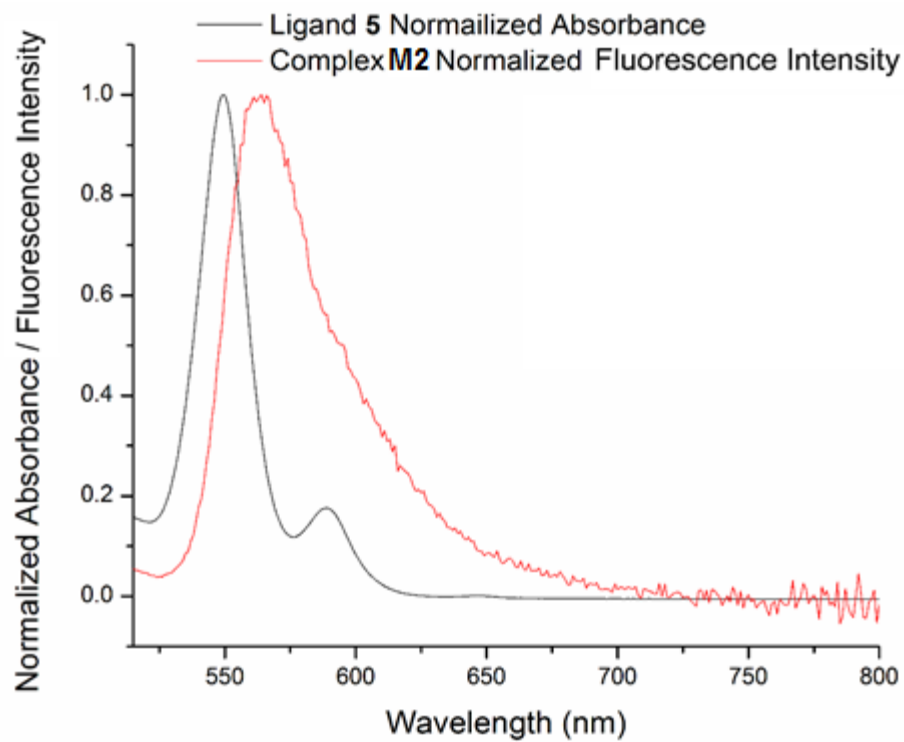
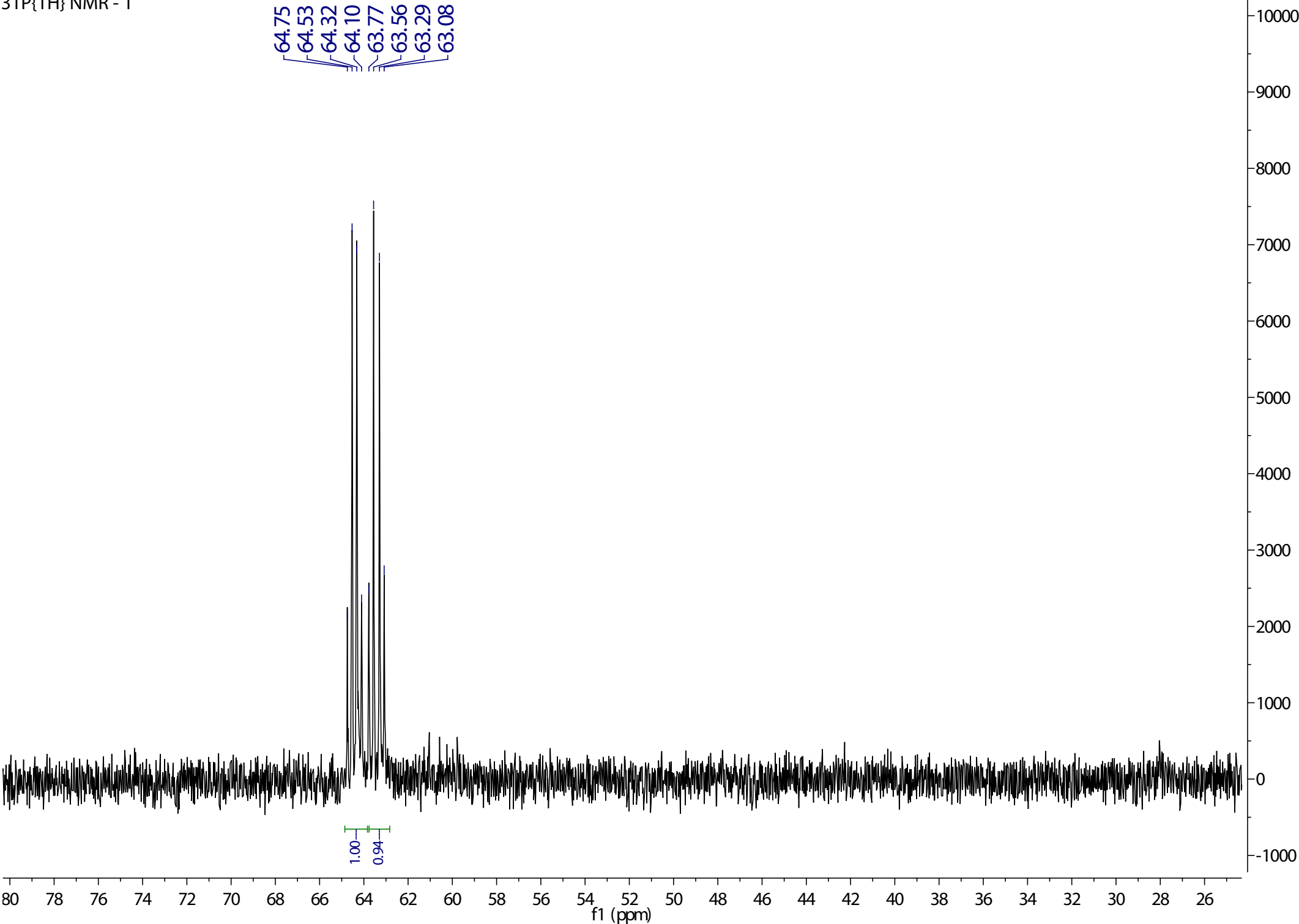
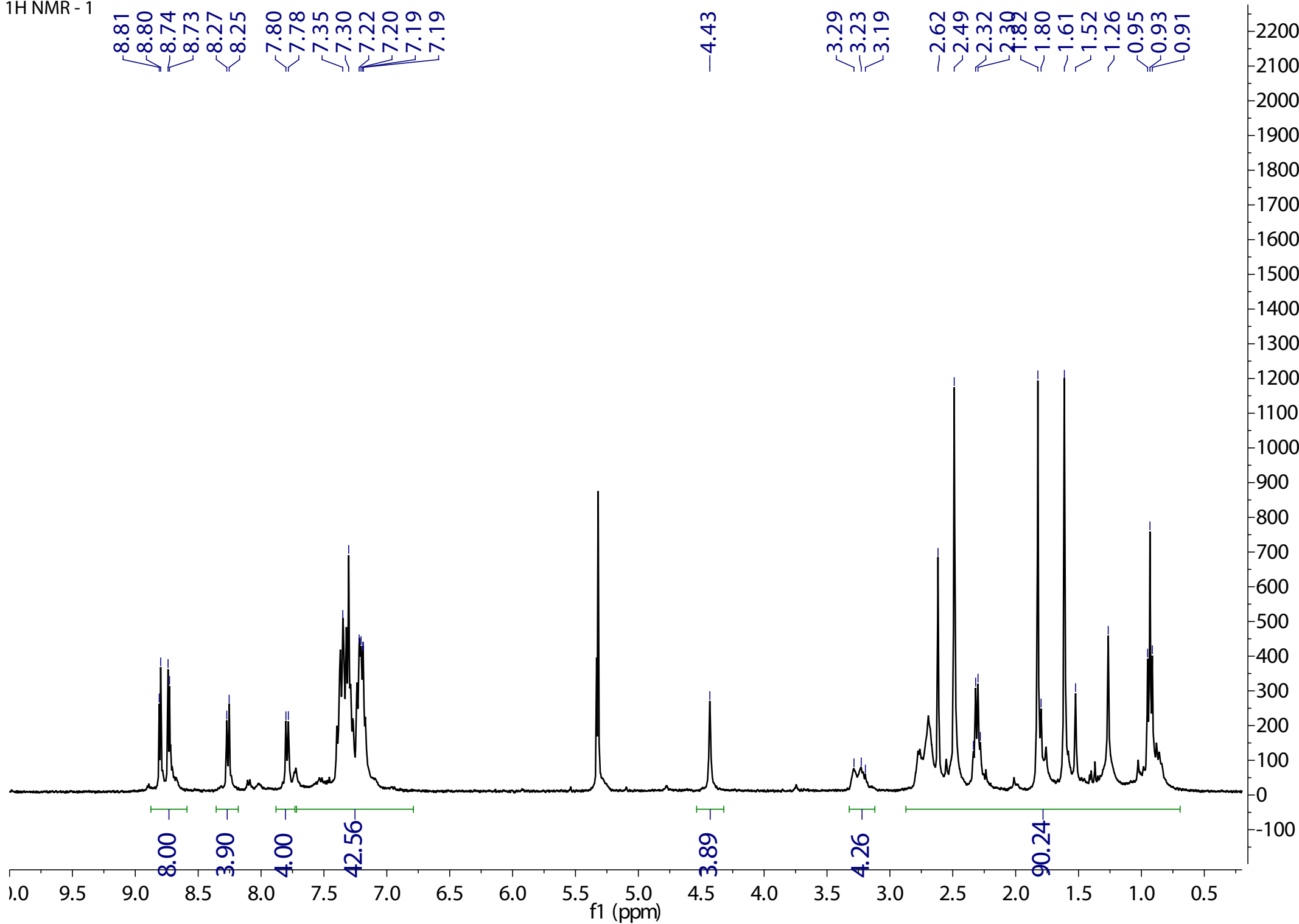
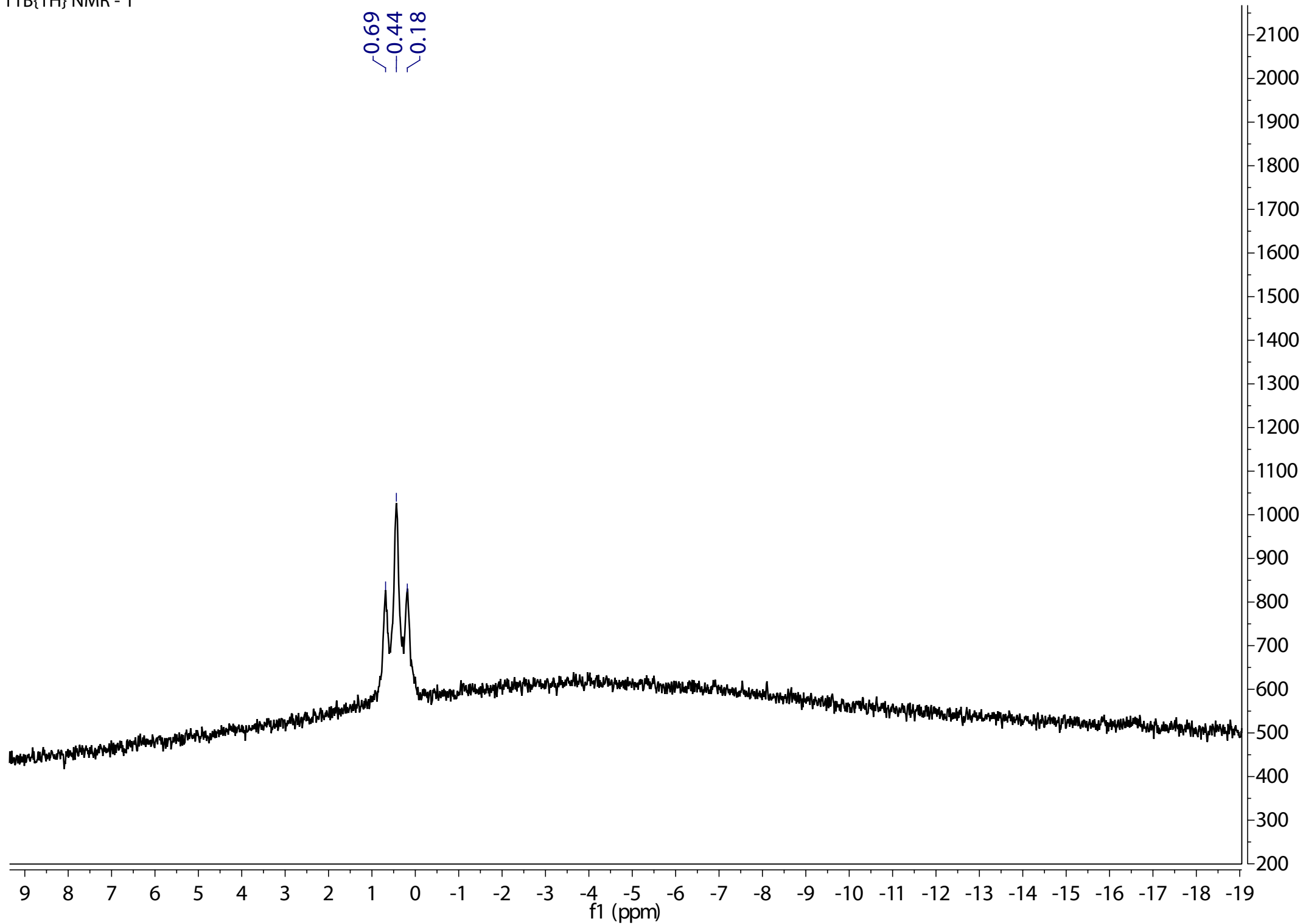
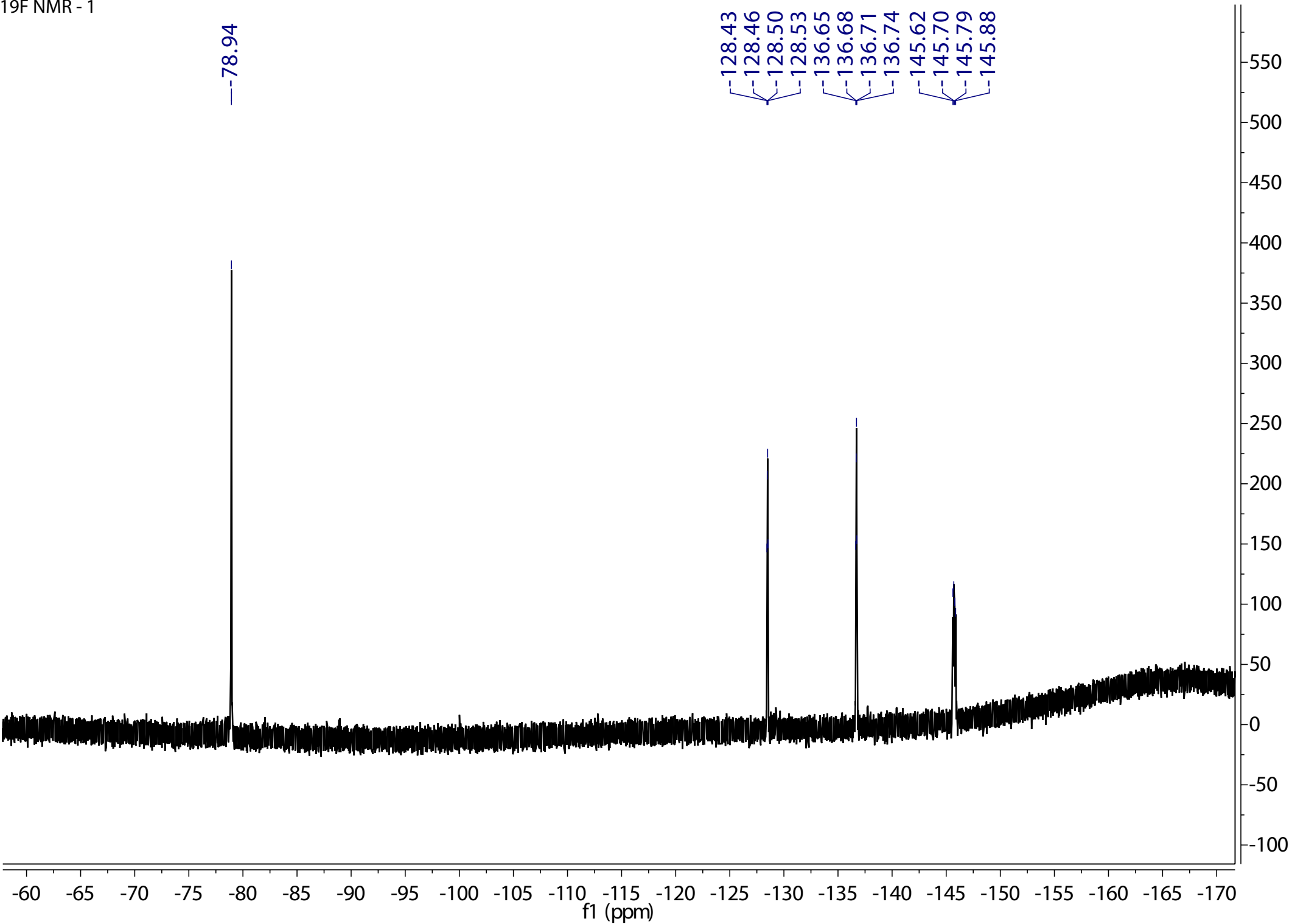


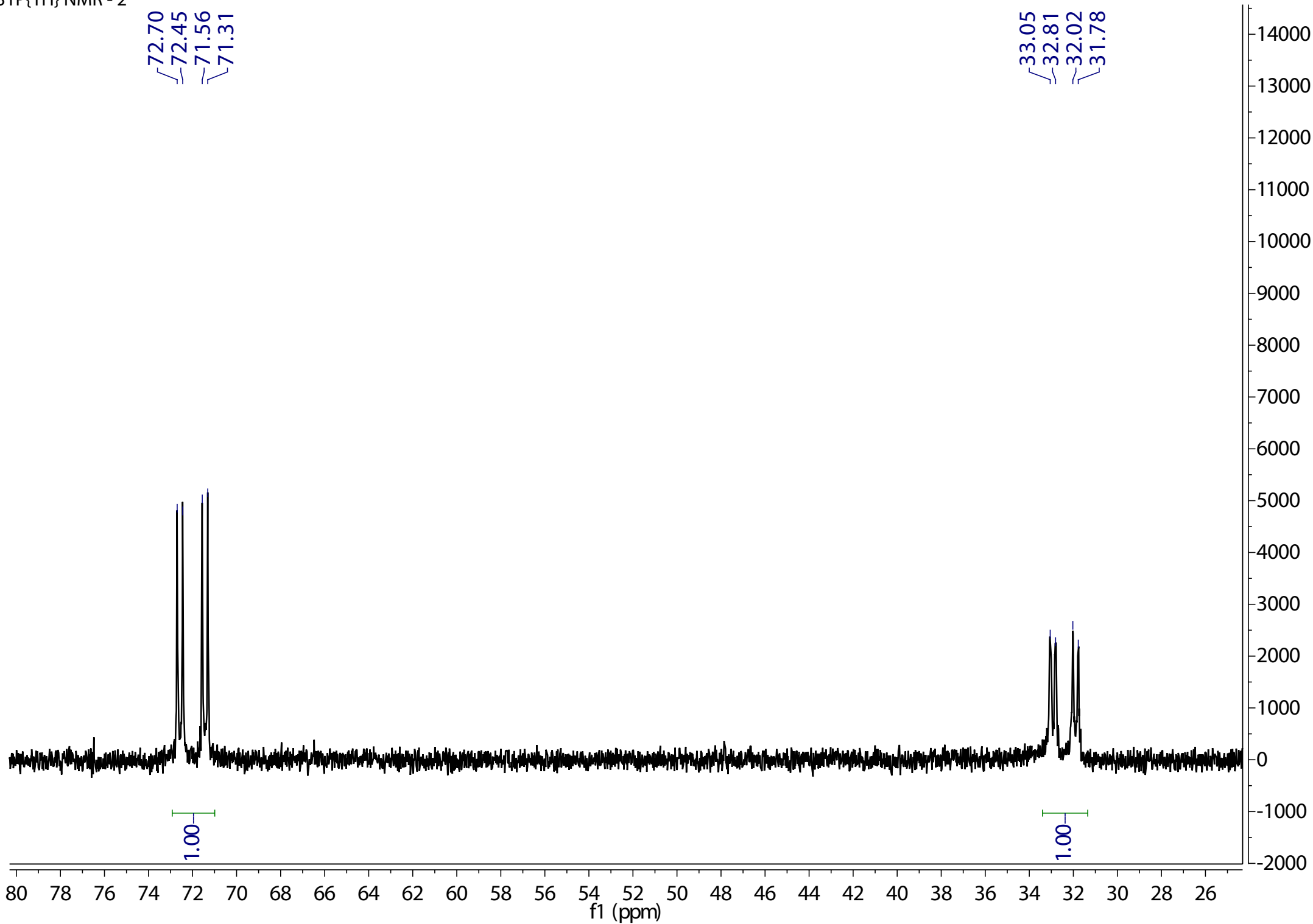
Figure S18. Normalized UV-vis spectrum of **5** and normalized fluorescence spectrum of **M2** in CH_2Cl_2 .





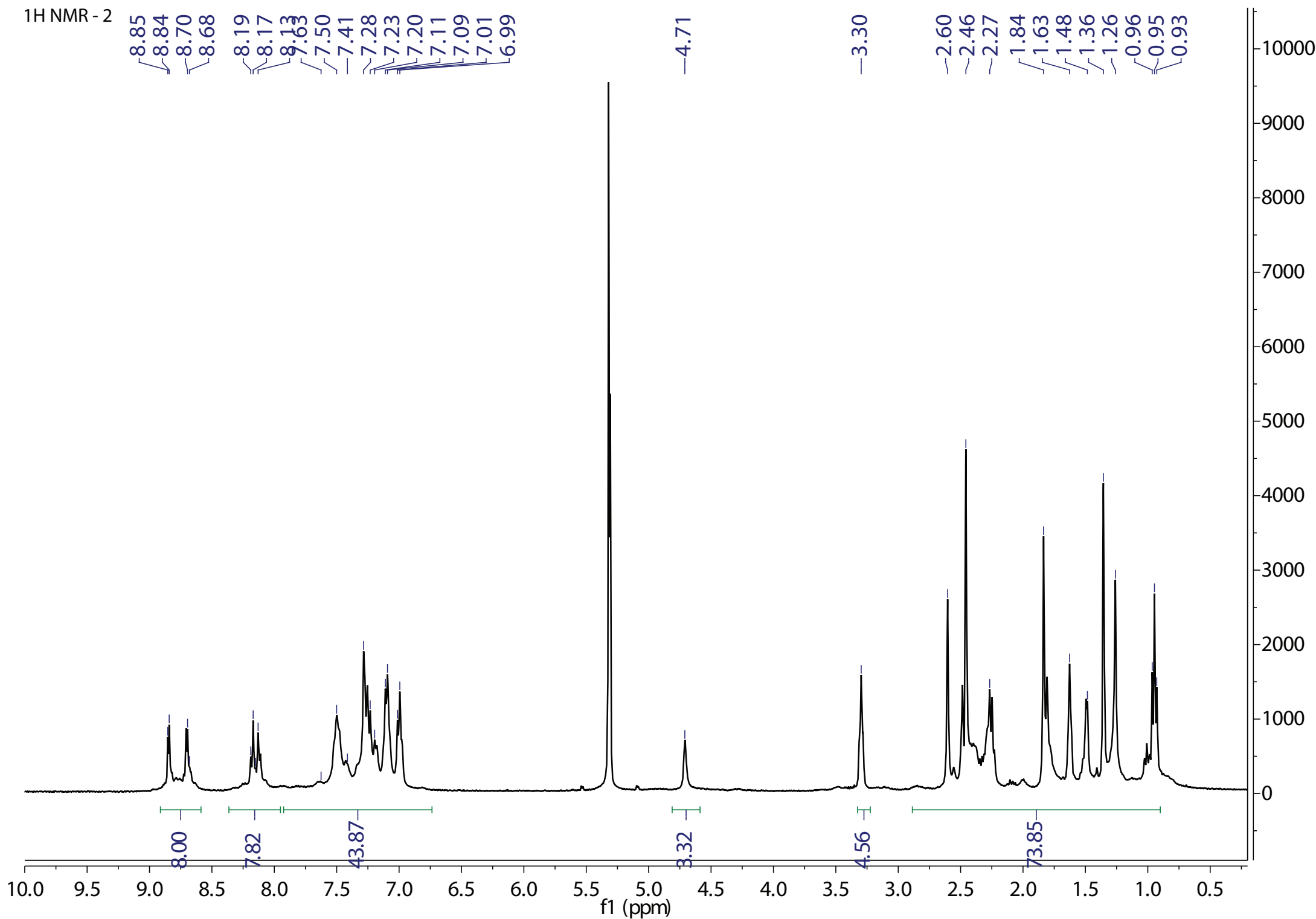


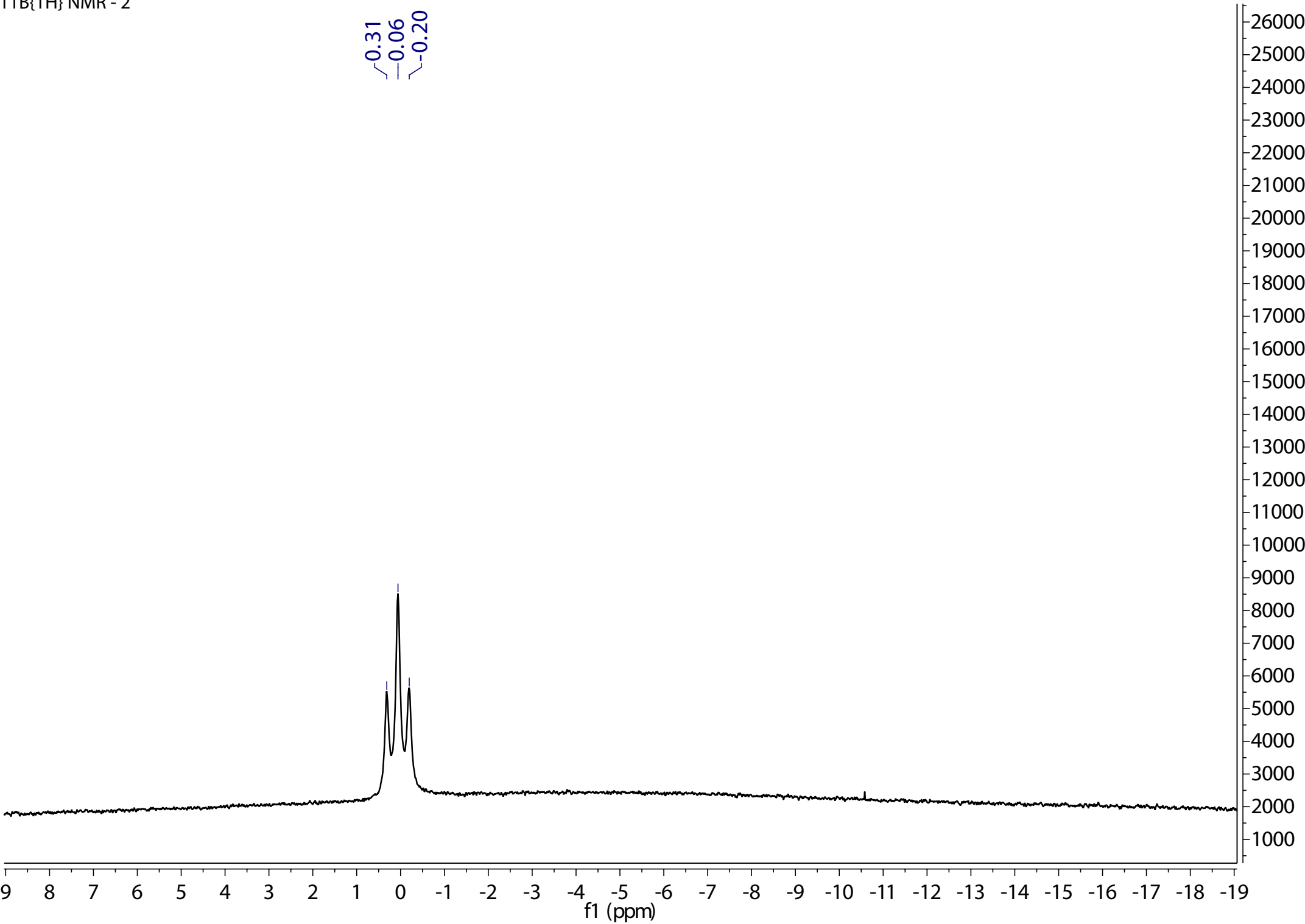




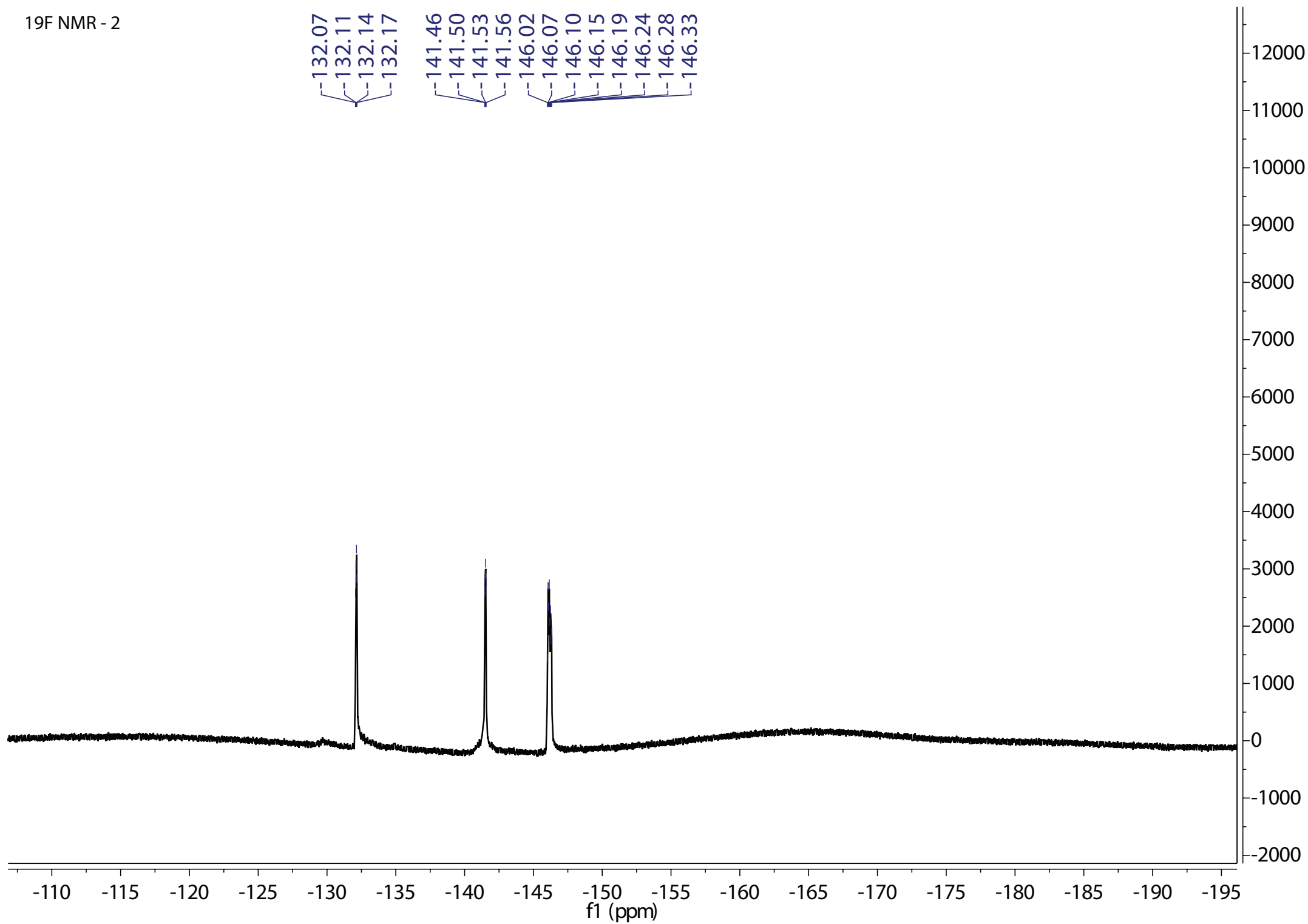
¹H NMR - 2

8.85 8.84 8.70 8.68 8.19 8.17 8.13 7.63 7.50 7.41 7.28 7.23 7.20 7.11 7.09 7.01 6.99 4.71 3.30 2.60 2.46 2.27 1.84 1.63 1.48 1.36 1.26 0.96 0.95 0.93





¹⁹F NMR - 2



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- (1) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463-1473.
- (2) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029-5036.
- (3) Lifschitz, A. M.; Young, R. M.; Mendez-Arroyo, J.; Roznyatovskiy, V. V.; McGuirk, C. M.; Wasielewski, M. R.; Mirkin, C. A. *Chem. Commun.* **2014**, *50*, 6850.